

# Polyethylene glycol-modified poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) counter electrodes for dye-sensitized solar cell

Xiaodan Yan · Lingzhi Zhang

Received: 24 January 2013 / Accepted: 4 April 2013 / Published online: 18 April 2013  
© Springer Science+Business Media Dordrecht 2013

**Abstract** Poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) counter electrodes, doped with polyethylene glycol (PEG) and acetylene black as binding and conductivity promoting agent, were prepared by a simple mixing method for dye-sensitized solar cell. The electrochemical properties of the electrodes were characterized by cyclic voltammetry, electrochemical impedance spectroscopy (EIS), and Tafel polarization curves. Using PEG dopant, the electrocatalytic activity of PEDOT:PSS electrode was much improved, and further improved by adding a small amount of conducting acetylene black (0.2 wt%). The DSSC cells, using the PEDOT:PSS electrode with PEG (5 wt%) dopant and the composite electrode with PEG (5 wt%)/acetylene black, exhibited an energy conversion efficiency of 3.57 and 4.39 %, comparable with 4.50 % of the commonly used Pt electrode under the same experimental conditions. These results demonstrate that PEG-modified PEDOT:PSS counter electrode is promising to replace the expensive Pt for low cost DSSC, especially to meet the large-scale fabrication demands.

**Keywords** Poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) · Polyethylene glycol · Acetylene black · Counter electrode · Dye-sensitized solar cell

## 1 Introduction

The dye-sensitized solar cell (DSSC) is a device to directly convert the solar energy to electric power, and has been widely investigated due to its low cost, simple fabrication process and high energy conversion efficiency [1]. A typical DSSC consists of a nano-porous  $\text{TiO}_2$  film adsorbed with dye, an iodide/tri-iodide redox electrolyte, and a counter electrode (CE). The CE plays an important role in DSSC especially in terms of energy conversion efficiency. Although commonly used Pt CE has high catalytic activity for tri-iodide reduction, it is a rare metal on earth and very expensive, which limits the large-scale production of DSSC. Therefore, cheap and efficient alternative materials have been intensively developed to replace Pt recently, such as carbon materials (graphite, carbon black, activated carbon, carbon nanotube, carbon dye, and fullerene) [2–7], conducting polymers (poly(3,4-ethylene dioxythiophene), polypyrrole, polyaniline) [8–13], and vary recently metallic compounds (metal carbides, metal nitrides, and metal sulfides) [14–19].

Poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) has emerged as a promising material for electrodes in optoelectronic devices, due to its high transparency in visible range, remarkable stability, and is environmentally friendly in terms of fabricating process [20–25]. However, the DSSC cells using pristine PEDOT:PSS as counter electrode have not shown satisfied performance so far due to the low short-circuit current ( $J_{\text{sc}}$ ) and fill factor (FF), which is mainly determined by the conductivity of PEDOT:PSS and the binding strength between PEDOT:PSS and substrate [26, 27]. To date, tremendous effort has been paid to address the issues mentioned above. Fan et al. [28] reported an energy conversion efficiency of 6.5 % using multiwall carbon nanotube

X. Yan · L. Zhang (✉)  
Key Laboratory of Renewable Energy and Gas Hydrate,  
Guangzhou Institute of Energy Conversion, Chinese Academy of  
Sciences, No. 2 Nengyuan Road, Guangzhou 510640,  
Guangdong, China  
e-mail: lzzhang@ms.giec.ac.cn

(CNT)/PEDOT:PSS composite CE in DSSC, which is close to that using the conventional Pt CE. Other carbon materials [29, 30], organic solvents [26], nanoparticles [31–33], and other conducting polymer (polypyrrol) [34] have also been added into PEDOT:PSS, aiming to improve the performance of PEDOT:PSS CE by increasing its conductivity and/or the surface area of the electrode.

Polyethylene glycol (PEG) is a water soluble polymer and has excellent film forming, emulsifying, and adhesive properties. It has been reported that the conductivity of PEDOT:PSS film can be improved an order of magnitude by doping with PEG and other alcohols [20, 35]. Furthermore, PEG can also serve as a binder to improve the mechanical properties of the electrodes. PEG-modified PEDOT:PSS film is expected to exhibit improved performance as counter electrode in DSSC. As far as we know, the electrochemical properties of the PEG-modified PEDOT:PSS has not been investigated as CE in DSSC.

In this work, we report the preparation of PEDOT:PSS films with different doping level (1, 5, 10 wt%) of PEG as counter electrodes by a simple mixing method for DSSC. To further enhance the conductivity and roughness of the counter electrode, a small amount of acetylene black (0.2 wt%) was doped in PEDOT:PSS film with PEG dopant. The electrochemical properties of the as-prepared electrodes are investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and Tafel polarization curves and compared with Pt electrode.

## 2 Experimental

### 2.1 Materials

Poly(3,4-ethylene dioxythiophene):poly(4-styrene sulfonate) aqueous solution (PEDOT:PSS, 1 wt% dispersion in water, PEDOT/PSS (w/w) = 1:2,  $10^4 - 10^6$  Ohm/sq) was obtained from Guangzhou AIBOT Synthetic Material Company (China); 4-*tert*-butylpyridine (TBP) was obtained from TCI (Japan); 3-methoxypropionitrile (MPN) was obtained from Alfa Aesar (England); The N3 dye (Ruthenium 535) was obtained from Solaronix SA (Switzerland); P25-TiO<sub>2</sub> was obtained from Degussa (Germany); Anhydrous LiI, I<sub>2</sub>, LiClO<sub>4</sub>, polyethylene glycol ( $M_w = 20000$ , PEG 20000), polyethylene glycol ( $M_w = 6000$ , PEG 6000) and acetonitrile were obtained from Aladdin (China) and used as received.

### 2.2 Preparation of counter electrodes

Poly(3,4-ethylene dioxythiophene):poly(4-styrene sulfonate) aqueous solution and different weight percentages of PEG 6000 (1, 5, 10 wt% with respect to PEDOT:PSS

aqueous solution) were mixed and fully grinded in an agate mortar. The mixed slurry was coated on FTO glass by doctor-blade technique to give PEG 6000-modified PEDOT:PSS films. The as-prepared counter electrodes were noted as PEG(1)–PEDOT:PSS, PEG(5)–PEDOT:PSS, and PEG(10)–PEDOT:PSS corresponding to the sample with different PEG contents in the electrodes. To further improve the conductivity and surface roughness of the counter electrodes, a composite CE was prepared by adding 0.2 wt% acetylene black (AB) in the formulation of PEG(5)–PEDOT:PSS electrode, and noted as PEG(5)–PEDOT:PSS/AB. All the prepared CEs were dried at 80 °C for 30 min in air. For comparison, Pt CE electrode (sputtered on FTO glass; Wuhan Geao Instruments & Technology Co., China) was also tested in the same conditions.

### 2.3 Fabrication of dye-sensitized solar cell

To prepare the mesoporous TiO<sub>2</sub> film, TiO<sub>2</sub> powder (1.2 g, P25 Degussa), 30 wt% PEG 20000 aqueous solution (1 mL), acetylacetone (0.04 mL) and distilled water (1 mL) were mixed and grinded. To the above mixture was then slowly added distilled water (1 mL) and Triton X-100 (0.02 mL) under continuous stirring for 10 min. Several drops of this suspension were spread onto the FTO glass using a glass rod to prepare TiO<sub>2</sub> film. The film was dried in air and sintered at 450 °C for 30 min and then cooled to 80 °C. The mesoporous TiO<sub>2</sub> electrode was immediately immersed in a solution of N3 dye in absolute ethyl alcohol overnight. The DSSC was fabricated with a TiO<sub>2</sub> electrode, a CE and an electrolyte containing 0.5 M LiI, 0.05 M I<sub>2</sub> and 0.5 M TBP in MPN. A portion of 0.2 cm<sup>2</sup> was selected as active area for DSSC photovoltaic performance test.

### 2.4 Measurements

The symmetrical dummy cell was sandwiched by two identical counter electrodes filling the electrolyte the same to the one used in fabricating DSSC. The active area of the dummy cell was 0.28 cm<sup>2</sup>. The (EIS) was tested with symmetrical cells in the dark using a CHI660D electrochemical workstation (Shanghai Chenhua Device Company, China) at frequencies ranging from 0.1 Hz to 1 M Hz. The bias of EIS test was set at 0 V, while the AC amplitude was set at 20 mV. Tafel polarization measurements were carried out in the symmetrical dummy cell similar to the one used in the EIS test. Cyclic voltammetry measurement was carried out in a 3-electrode system with the CHI660D electrochemical workstation. The PEDOT:PSS electrode (or PEG 6000-modified PEDOT:PSS electrode) served as a working electrode, Pt served as a counter electrode, and Ag/AgCl (sat'd KCl) served as a reference electrode. The electrolyte contained 0.1 M

$\text{LiClO}_4$ , 10 mM  $\text{LiI}$ , and 1 mM  $\text{I}_2$  in acetonitrile. The scan rate was set at  $10 \text{ mV s}^{-1}$ . The photocurrent density–voltage ( $J$ – $V$ ) curves of the DSSCs with different counter electrodes were obtained using the CHI660D electrochemical workstation. A 150 W Xe arc lamp with an AM 1.5 solar simulating filter served as the light source. The light intensity was adjusted to  $100 \text{ mW cm}^{-2}$  using a reference Si solar cell.

### 3 Results and discussion

#### 3.1 Electrochemical performance of PEDOT:PSS electrodes

##### 3.1.1 Electrochemical impedance results

Electrochemical impedance spectroscopy (EIS) measurements were carried out to characterize the catalytic activity of the pristine PEDOT:PSS and modified PEDOT:PSS CEs for the reduction of tri-iodide. Figure 1 showed the Nyquist plots of dummy cells prepared by PEDOT:PSS CEs. The values of  $R_s$  and  $R_{ct}$  were obtained by fitting the semicircles at high frequency range (leftmost semicircle) in the Nyquist plots to the equivalent circuit (Fig. 1).  $R_s$  is introduced to describe the ohmic resistance of the load and the conducting substrates.  $R_{ct}$  represents the charge transfer resistance of the tri-iodide reduction at the interface of electrode/electrolyte. CPE/W refers to the double layer capacitance and the Nernst diffusion impedance of the tri-iodide/iodide redox couple in the electrolyte, respectively [4, 18, 36].

The values of  $R_s$  and  $R_{ct}$  were shown in Table 1. Pt electrode showed the smallest  $R_s$  value, which reflects the best binding strength between Pt and the substrate [4]. For

**Table 1** Electrochemical impedance spectroscopy EIS parameters of the dummy cells fabricated with different counter electrodes

Counter electrode	$R_s$ ( $\Omega \text{ cm}^2$ )	$R_{ct}$ ( $\Omega \text{ cm}^2$ )
Pt	5.61	3.45
PEDOT:PSS	10.46	6.81
PEG(1)-PEDOT:PSS	10.34	4.61
PEG(5)-PEDOT:PSS	11.00	2.59
PEG(10)-PEDOT:PSS	14.22	1.99
PEG(5)-PEDOT:PSS/AB	11.75	0.85

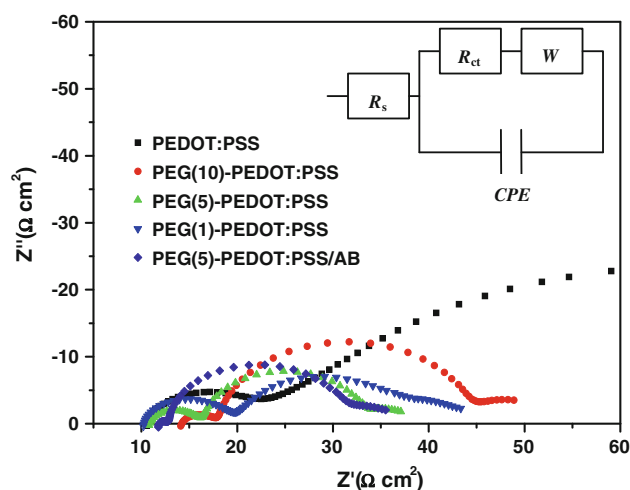
PEG(1)–PEDOT:PSS electrode with 1 wt% PEG dopant,  $R_s$  value ( $10.34 \Omega \text{ cm}^2$ ) decreased slightly compared with the pristine PEDOT:PSS electrode ( $10.46 \Omega \text{ cm}^2$ ). When increasing PEG content to 5/10 wt%, the  $R_s$  value increased to 11.00/14.22  $\Omega \text{ cm}^2$ , correspondingly. While the  $R_{ct}$  value decreased from 4.61 to 1.99  $\Omega \text{ cm}^2$  for the sample with 1 and 10 wt% PEG dopant. All PEG-modified PEDOT:PSS electrodes showed a smaller  $R_{ct}$  than that of pristine PEDOT:PSS CE ( $6.81 \Omega \text{ cm}^2$ ), implying that the electrocatalytic activity at electrode/electrolyte for tri-iodide/iodide redox reaction was improved by adding PEG into PEDOT:PSS. For the PEG(5)–PEDOT:PSS electrode showed the lowest  $R_{ct}$  and a relatively low  $R_s$ , it was chosen for our next study.

Acetylene black (0.2 wt% with respect to the 5 wt% PEG-modified PEDOT:PSS solution) was added to further improve the conductivity and active surface area of the CE films. For the PEG(5)–PEDOT:PSS/AB electrode,  $R_s$  value ( $11.75 \Omega \text{ cm}^2$ ) increased slightly compared with the PEG(5)–PEDOT:PSS electrode ( $11.00 \Omega \text{ cm}^2$ ). While the  $R_{ct}$  value decreased significantly from 2.59 to 0.85  $\Omega \text{ cm}^2$  for the PEG(5)–PEDOT:PSS electrode and the PEG(5)–PEDOT:PSS/AB electrode, implying that charge transfer rate was further improved by adding a small amount of AB.

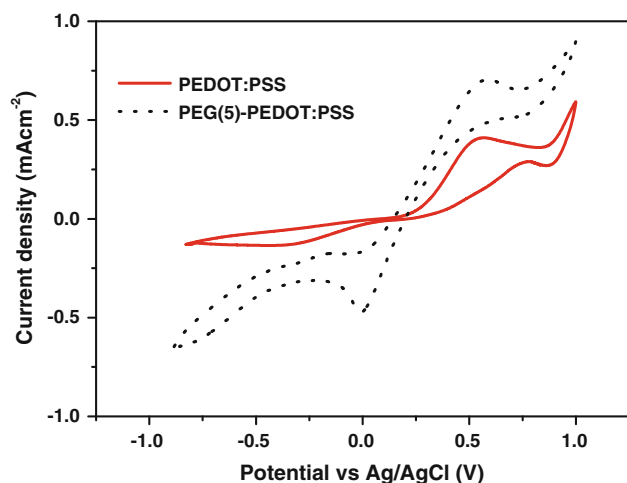
Compared with sputtered Pt electrode, the PEG(5)–PEDOT:PSS/AB electrode has a smaller  $R_{ct}$  value and a larger  $R_s$  value. This indicates that the PEG(5)–PEDOT:PSS/AB electrode has higher charge transfer rate and better catalytic activity but poorer binding strength between active materials and the FTO substrate than Pt [4].

##### 3.1.2 Cyclic voltammetry results

Cyclic voltammetry (CV) results of PEDOT:PSS and PEG(5)–PEDOT:PSS counter electrodes were shown in Fig. 2. Typically, tri-iodide/iodide redox reaction displays two pairs of oxidation and reduction peaks, where the relatively negative/positive redox pair can be assigned to the Eq. (1)/(2), respectively [37]. Only one pair of redox peak was observed for PEDOT:PSS and PEG(5)–PEDOT:PSS electrodes assigned to the Eq. (1). The pristine PEDOT:PSS electrode did not show well-defined peaks



**Fig. 1** Electrochemical impedance spectroscopy (EIS) spectra of the dummy cells fabricated with two identical counter electrodes. Inset is the equivalent circuit diagram of the dummy cells



**Fig. 2** Cyclic voltammograms of PEDOT:PSS and PEG(5)-PEDOT:PSS counter electrodes at a scan rate of  $10 \text{ mV s}^{-1}$

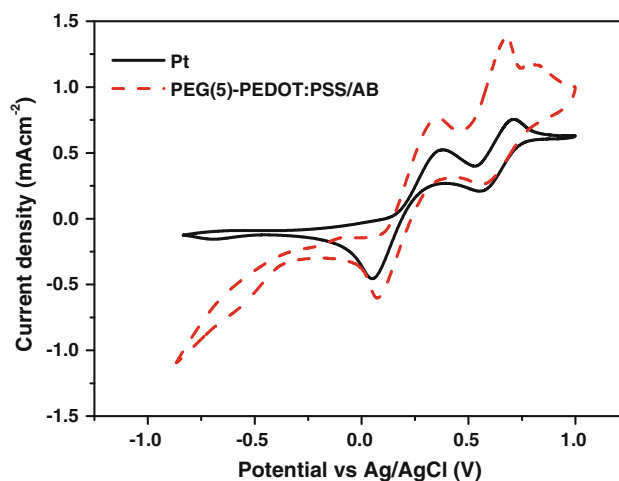
due to low reduction reaction rate. While the PEG(5)-PEDOT:PSS electrode presented a sharp and clear reduction peak of tri-iodide, indicating an enhanced electrochemical activity for the PEG-modified PEDOT:PSS electrode, which is consistent with EIS results.



Figure 3 showed the CV results of PEG(5)-PEDOT:PSS/AB electrode and sputtered Pt electrode for comparison. Two typical pairs of oxidation and reduction peaks of tri-iodide/iodide redox reaction were observed for Pt and PEG(5)-PEDOT:PSS/AB electrodes. PEG(5)-PEDOT:PSS/AB composite electrode exhibited a similar peak potential to Pt. In theory, the value of peak separation ( $\Delta E_p$ ) varies inversely with charge transfer rate [18]. The value of  $\Delta E_p$  is 0.331 V for Pt and 0.286 V for PEG(5)-PEDOT:PSS/AB electrode. This indicates that PEG(5)-PEDOT:PSS/AB electrode has somewhat higher charge transfer rate and better catalytic activity than Pt. Furthermore, PEG(5)-PEDOT:PSS/AB electrode shows a larger current density than that of Pt at the same potential, which demonstrates that PEG(5)-PEDOT:PSS/AB could provide more catalytic sites due to its larger active surface area [32]. However, the PEG(5)-PEDOT:PSS/AB electrode exhibited a slightly lower efficiency than Pt, probably due to the poor contact between the composite and FTO substrate as analyzed in the EIS results.

### 3.1.3 Tafel results

Tafel polarization measurements were carried out to confirm the electrochemical catalytic activity of the electrodes (Fig. 4). The exchange current density ( $J_0$ ) and the limiting diffusion current density ( $J_{\text{lim}}$ ) are important parameters to



**Fig. 3** Cyclic voltammograms of Pt and PEG(5)-PEDOT:PSS/AB counter electrodes at a scan rate of  $10 \text{ mV s}^{-1}$

reflect catalytic activity of the electrode.  $J_0$  is inverse proportion to  $R_{\text{ct}}$  according to Eq. (3) and can be obtained from the slope of the curve.  $J_{\text{lim}}$  depends on the diffusion of the tri-iodide species in the electrolyte according to Eq. (4) and can be obtained from the curve in the high potential zone [38].

$$J_0 = \frac{RT}{nFR_{\text{ct}}} \quad (3)$$

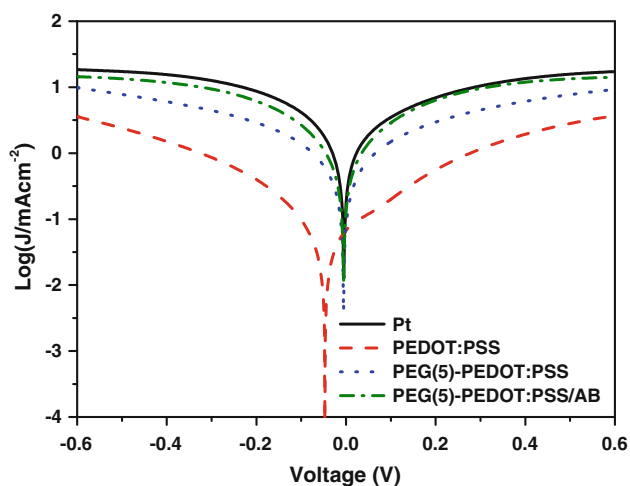
$$D = \frac{l}{2nFC} J_{\text{lim}} \quad (4)$$

where  $R$  is the gas constant,  $T$  is the temperature,  $F$  is Faraday's constant,  $n$  is the number of electrons involved in the reduction of tri-iodide at the electrode,  $R_{\text{ct}}$  is the charge transfer resistance,  $D$  is the diffusion coefficient of the tri-iodide,  $l$  is the spacer thickness,  $C$  is the tri-iodide concentration.

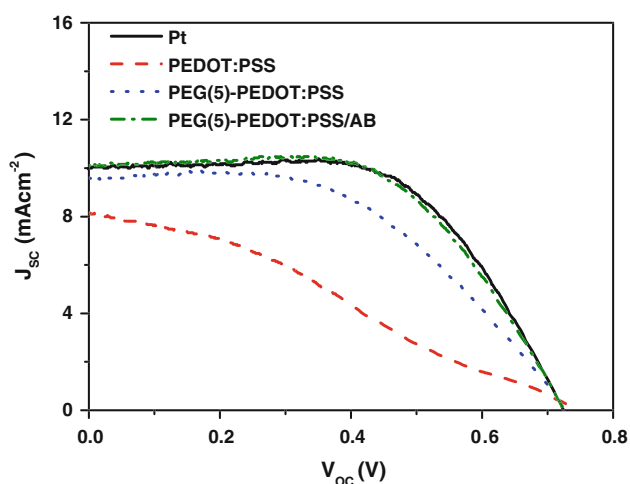
The curve of pristine PEDOT:PSS electrode exhibited a gentle slope and the lowest  $J_{\text{lim}}$  value, demonstrating its worst catalytic activity for the reduction of tri-iodide. The  $J_{\text{lim}}$  values for three other electrodes are at the same magnitude except for PEDOT:PSS electrode, indicating that these three electrodes have a similar diffusion coefficient. In addition, the slope for the composite electrode of PEG(5)-PEDOT:PSS/AB is close to Pt, thus a similar  $J_0$  for the composite electrode and Pt. Therefore, the catalytic activity of PEG(5)-PEDOT:PSS/AB electrode is comparable to that of Pt for reduction of tri-iodide. In short, the catalytic activity of PEDOT:PSS electrodes was much improved by adding PEG and further improved by adding a small amount of conducting AB.

### 3.2 Photovoltaic performance of DSSCs

The photocurrent density–voltage ( $J$ – $V$ ) curves of DSSCs based on different CEs measured under the illumination of



**Fig. 4** Tafel polarization curves of the dummy cells based on different counter electrodes



**Fig. 5** Characteristic photocurrent density–voltage ( $J$ – $V$ ) curves of DSSCs based on different counter electrodes

1 sun were shown in Fig. 5. The photovoltaic performance parameters of the DSSCs such as the short-circuit current ( $J_{SC}$ ), the open-circuit voltage ( $V_{OC}$ ), FF, and the energy conversion efficiency ( $\eta$ ) were summarized in Table 2. For the pristine PEDOT:PSS counter electrode,  $J_{SC}$  and FF are very low due to the poor electrocatalytic activity, giving a

**Table 2** The photovoltaic performance parameters of the DSSCs made of different counter electrodes

Counter electrode	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (V)	FF	$\eta$ (%)
Pt	10.00	0.724	0.6215	4.50
PEDOT:PSS	8.14	0.744	0.3022	1.83
PEG(5)-PEDOT:PSS	9.58	0.730	0.5105	3.57
PEG(5)-PEDOT:PSS/AB	10.11	0.726	0.5981	4.39

poor efficiency of 1.83 %. By adding PEG as a conductivity promoting agent and binding agent, PEG(5)–PEDOT:PSS sample showed a much improved energy conversion efficiency of 3.57 %. The cell using the composite CE of PEG(5)–PEDOT:PSS/AB yielded an energy conversion efficiency of 4.39 %, comparable to that of Pt-based cell (4.50 %), which is reflected from its high  $J_{SC}$  and FF. Apparently, PEG played a role in enhancing conductivity of PEDOT:PSS electrodes; AB (0.2 wt%) component in the composite electrode further increased the catalytic activity as expected.

## 4 Conclusions

We successfully prepared PEG-modified PEDOT:PSS films as counter electrodes for DSSC. CV, EIS and Tafel measurements showed that the electrocatalytic activity for tri-iodide/iodide redox reaction was much improved by adding PEG into PEDOT:PSS as a conductivity promoting agent and binding agent, and further improved by adding a small amount of conducting acetylene black. The DSSC using PEG(5)–PEDOT:PSS/AB composite as counter electrode exhibited an energy conversion efficiency of 4.39 %, comparable with the commonly used Pt (4.50 %). These results demonstrate that PEG-modified translucent PEDOT:PSS films are promising materials to replace the expensive Pt as CEs for low cost DSSC, especially to meet the large-scale fabrication demands.

**Acknowledgments** This work was supported by the National Science Foundation of China (50973113) and the Hundred Talents Program of Chinese Academy of Sciences.

## References

- O'Regan B, Grätzel M (1991) A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO<sub>2</sub> films. *Nature* 353:737–740
- Kay A, Grätzel M (1996) Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder. *Sol Energy Mater Sol Cells* 44:99–117
- Murakami TN, Ito S, Wang Q, Nazeeruddin MK, Bessho T, Cesar I, Liska P, Baker RH, Comte P, Péchy P, Grätzel M (2006) Highly efficient dye-sensitized solar cells based on carbon black counter electrodes. *J Electrochem Soc* 153:A2255–A2261
- Wu M, Lin X, Wang T, Qiu J, Ma T (2011) Low-cost dye-sensitized solar cell based on nine kinds of carbon counter electrodes. *Energy Environ Sci* 4:2308–2315
- Cha SI, Koo BK, Seo SH, Lee DY (2010) Pt-free transparent counter electrodes for dye-sensitized solar cells prepared from carbon nanotube micro-balls. *J Mater Chem* 20:659–662
- Denaro T, Baglio V, Girolamo M, Antonucci V, Arico AS, Matteucci F, Ornelas R (2009) Investigation of low cost carbonaceous materials for application as counter electrode in dye-sensitized solar cells. *J Appl Electrochem* 39:2173–2179



7. Han J, Kim H, Kim DY, Jo SM, Jang SY (2010) Water-soluble polyelectrolyte-grafted multiwalled carbon nanotube thin films for efficient counter electrode of dye-sensitized solar cells. *ACS Nano* 4:3503–3509
8. Sakurai S, Jiang H, Takahashi M, Kobayashi K (2009) Enhanced performance of a dye-sensitized solar cell with a modified poly(3,4-ethylenedioxythiophene)/TiO<sub>2</sub>/FTO counter electrode. *Electrochim Acta* 54:5463–5469
9. Lee KM, Chiu WH, Wei HY, Hu CW, Suryanarayanan V, Hsieh WF, Ho KC (2010) Effects of mesoscopic poly(3,4-ethylenedioxythiophene) films as counter electrodes for dye-sensitized solar cells. *Thin Solid Films* 518:1716–1721
10. Lee KM, Chen PY, Hsu CY, Huang JH, Ho WH, Chen HC, Ho KC (2009) A high-performance counter electrode based on poly(3,4-alkylenedioxythiophene) for dye-sensitized solar cells. *J Power Sour* 188:313–318
11. Ameen S, Akhtar MS, Kim YS, Yang OB, Shin HS (2010) Sulfamic acid-doped polyaniline nanofibers thin film-based counter electrode: application in dye-sensitized solar cells. *J Phys Chem C* 114:4760–4764
12. Nagai H, Segawa H (2004) Energy-storable dye-sensitized solar cell with a polypyrrole electrode. *Chem Commun* 8:974–975
13. Wu J, Li Q, Fan L, Lan Z, Li P, Lin J, Hao S (2008) High-performance polypyrrole nanoparticles counter electrode for dye-sensitized solar cells. *J Power Sources* 181:172–176
14. Wu M, Lin X, Hagfeldt A, Ma T (2011) Low-cost molybdenum carbide and tungsten carbide counter electrodes for dye-sensitized solar cells. *Angew Chem Int Ed* 50:3520–3524
15. Wu M, Lin X, Wang Y, Wang L, Guo W, Qi D, Peng X, Hagfeldt A, Grätzel M, Ma T (2012) Economical Pt-free catalysts for counter electrodes of dye-sensitized solar cells. *J Am Chem Soc* 134:3419–3428
16. Jiang QW, Li GR, Gao XP (2009) Highly ordered TiN nanotube arrays as counter electrodes for dye-sensitized solar cells. *Chem Commun* 44:6720–6722
17. Hu Y, Zheng Z, Jia H, Tang Y, Zhang L (2008) Selective synthesis of FeS and FeS<sub>2</sub> nanosheet films on Iron substrates as novel photocathodes for tandem dye-sensitized solar cells. *J Phys Chem C* 112:13037–13042
18. Wang M, Anghel AM, Marsan B, Cevey Ha NL, Postrakulchote N, Zakeeruddin SM, Grätzel M (2009) CoS supersedes Pt as efficient electrocatalyst for triiodide reduction in dye-sensitized solar cells. *J Am Chem Soc* 131:15976–15977
19. Sun H, Qin D, Huang S, Guo X, Li D, Luo Y, Meng Q (2011) Dye-sensitized solar cells with NiS counter electrodes electrodeposited by a potential reversal technique. *Energy Environ Sci* 4:2630–2637
20. Groenendaal LB, Jonas F, Freitag D, Pielartzik H, Reynolds JR (2000) Poly(3,4-ethylenedioxythiophene) and its derivatives: past, present, and future. *Adv Mater* 12:481–494
21. Ouyang BY, Chi CW, Chen FC, Xu Q, Yang Y (2005) High-conductivity poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) film and its application in polymer optoelectronic devices. *Adv Funct Mater* 15:203–208
22. Zhang C, Wang K, Hu L, Kong F, Guo L (2007) Improved performance of solid-state dye-sensitized solar cells with *p/p*-type nanocomposite electrolyte. *J Photochem Photobiol A Chem* 189:329–333
23. Biancardo M, West K, Krebs FC (2007) Quasi-solid-state dye-sensitized solar cells: Pt and PEDOT:PSS counter electrodes applied to gel electrolyte assemblies. *J Photochem Photobiol A* 187:395–401
24. Chang C-C, Jiang M-T, Chang C-L, Lin C-L (2011) Preparation and characterization of poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) composite thin films highly loaded with platinum nanoparticles. *Mater Chem Phys* 127:440–445
25. Shibata Y, Kato T, Kado T, Shiratuchi R, Takashima W, Kaneto K, Hayase S (2003) Quasi-solid dye sensitised solar cells filled with ionic liquid-increase in efficiencies by specific interaction between conductive polymers and gelators. *Chem Commun* 9:2730–2731
26. Chen JG, Wei HY, Ho KC (2007) Using modified poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate) film as a counter electrode in dye-sensitized solar cells. *Sol Energy Mater Sol Cells* 91:1472–1477
27. Xia J, Masaki N, Jiang K, Yanagida S (2007) The influence of doping ions on poly(3,4-ethylenedioxythiophene) as a counter electrode of a dye-sensitized solar cell. *J Mater Chem* 17:2845–2850
28. Fan B, Mei X, Sun K, Ouyang J (2008) Conducting polymer/carbon nanotube composite as counter electrode of dye-sensitized solar cells. *Appl Phys Lett* 93:143103
29. Hong W, Xu Y, Lu G, Li C, Shi G (2008) Transparent graphene/PEDOT-PSS composite films as counter electrodes of dye-sensitized solar cells. *Electrochem Commun* 10:1555–1558
30. Yue G, Wu J, Xiao Y, Lin J, Huang M (2012) Low cost poly(3,4-ethylenedioxythiophene):polystyrenesulfonate/carbon black counter electrode for dye-sensitized solar cells. *Electrochim Acta* 67:113–118
31. Yeh MH, Lin LY, Lee CP, Wei HY, Chen CY, Wu CG, Vittala R, Ho KC (2011) A composite catalytic film of PEDOT:PSS/TiN-NPs on a flexible counter-electrode substrate for a dye-sensitized solar cell. *J Mater Chem* 21:19021–19029
32. Xu H, Zhang X, Zhang C, Liu Z, Zhou X, Pang S, Chen X, Dong S, Zhang Z, Zhang L, Han P, Wang X, Cui G (2012) Nanostructured titanium nitride/PEDOT:PSS composite films as counter electrodes of dye-sensitized solar cells. *ACS Appl Mater Interfaces* 4:1087–1092
33. Maiaugree W, Pimanpang S, Towannang M, Saekow S, Jarernboon W, Amornkitbamrung V (2012) Optimization of TiO<sub>2</sub> nanoparticle mixed PEDOT-PSS counter electrodes for high efficiency dye sensitized solar cell. *J Non-Cryst Solids* 358:2489–2495
34. Yue G, Wu J, Xiao Y, Lin J, Huang M, Lan Z (2010) Application of poly(3,4-ethylenedioxythiophene):polystyrenesulfonate/polypyrrole counter electrode for dye-sensitized solar cells. *J Phys Chem C* 114:4760–4764
35. Crispin X, Jakobsson FLE, Crispin A, Grim PCM, Andersson P, Volodin A, Haesendonck C, Auweraer MV, Salaneck WR, Berggren M (2006) The origin of the high conductivity of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) plastic electrodes. *Chem Mater* 18:4354–4360
36. Wei T-C, Chi-Chao Wan C-C, Wang Y-Y, Chen C, Shiu H (2007) Immobilization of Poly(*N*-vinyl-2-pyrrolidone)-capped platinum nanoclusters on indium-tin oxide glass and its application in dye-sensitized solar cells. *J Phys Chem C* 111:4847–4853
37. Popov AI, Geske DH (1958) Studies on the chemistry of halogen and of polyhalides. XIII. Voltammetry of iodine species in acetonitrile. *J Am Chem Soc* 80:1340–1352
38. Wu M, Lin X, Hagfeldt A, Ma T (2011) A novel catalyst of WO<sub>2</sub> nanorod for the counter electrode of dye-sensitized solar cells. *Chem Commun* 47:4535–4537